

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 207 050 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
22.05.2002 Bulletin 2002/21

(51) Int Cl.<sup>7</sup>: **B44C 1/175, B41M 5/00**

(21) Application number: **01309257.2**

(22) Date of filing: **31.10.2001**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR**  
Designated Extension States:  
**AL LT LV MK RO SI**

(30) Priority: **31.10.2000 US 702415**

(71) Applicant: **International Imaging Materials Inc.  
Amherst, NY 14228 (US)**

(72) Inventors:  
• **Geddes, Pamela A.**  
**Alden, New York 14004 (US)**  
• **Briggs, Barry J.**  
**Kelowna, British Columbia V1Z 3R3 (CA)**  
• **Harrison, Daniel J.**  
**Pittsford, New York 14534 (US)**

(74) Representative: **Powell, Stephen David et al  
WILLIAMS, POWELL & ASSOCIATES  
4 St Paul's Churchyard  
London EC4M 8AY (GB)**

(54) **Thermal transfer system for fired ceramic decals**

(57) A process for preparing a ceramic decal in which a printed image is applied to a backing sheet, and a covercoating is then applied to the printed substrate. A digitally printed ceramic colorant image is applied to the backing sheet; metal oxide colorant with a refractive index of greater than about 1.6 is used as the colorant.

Thereafter, the printed image is covercoated with an overcoat containing frit and binder. The total amount of frit applied in the process divided by the total amount of colorant used is at least 2, and the frit used has a melting temperature of at least 550 degrees Centigrade.

**EP 1 207 050 A2**

**Description**Field of the invention

[0001] A dry thermal printing process for printing a color image to a backing sheet which thereafter can be utilized to transfer the image to a ceramic substrate.

Background of the invention

[0002] Processes for preparing "decals" are well known. Thus, in United States patent 5,132,165 of Louis A. Blanco, a wet printing technique was described comprising the step of offset printing a first flux layer onto a backing sheet, forming a wet ink formulation free of glass and including a liquid printing vehicle and oxide coloring agent, wet printing the wet ink formulation onto the first flux layer to form a design layer, and depositing a second flux layer onto the design layer.

[0003] Digital printing methodologies offer a more convenient and lower cost method of mass customization of ceramic articles than do conventional analog printing methodologies, but they cannot be effectively utilized by the process of the Blanco patent.

[0004] The Blanco patent issued in July of 1992. In September of 1997, United States patent 5,665,472 issued to Konsuke Tanaka. This patent described a dry printing process which overcame some of the disadvantages of the Blanco process. However, the Tanaka process suffers from several major disadvantages.

[0005] When one attempts to use the process of the Tanaka patent to transfer images from a backing sheet to solid ceramic substrates (such as glass, porcelain, ceramic whitewares, etc.), one must use a temperature in excess of 550 degrees Celsius to effectively transfer an image which is durable. However, when such a transfer temperature is used with the Tanaka process, a poor image comprised with a multiplicity of surface imperfections (such as bubbles, cracks, voids, etc.) is formed. Furthermore, when the Tanaka process is used to attempt to transfer color images, a poor image with low color density and poor durability is formed. The Tanaka process is not useful for printing color images on most solid ceramic substrates.

[0006] It is an object of this invention to provide a digital process for preparing a decal for transferring images to a ceramic substrate which can effectively and durably transfer an image with improved optical properties.

Summary of the invention

[0007] In accordance with this invention, there is provided a digital process for preparing a ceramic decal. In one step of this process, a digitally printed ceramic colorant image is applied to a coated backing sheet utilizing a specified colorant. A flux covercoat is digitally printed to the assembly either before or after the ceramic colorant image has been applied; the covercoat contains

both frit and binder, and the frit has a melting temperature of at least 550 degrees Centigrade. The total amount of frit applied to the backing sheet in this process is at least 2 times as great as the total amount of colorant used in the process.

Brief description of the drawings

[0008] The invention will be described by reference to this specification and the attached drawings, in which like numerals refer to like elements, and in which:

Figure 1 is a schematic representation of a ceramic substrate to which a color image has been transferred in accordance with the invention;

Each of Figures 2, 3, 4, 5, and 6 is a schematic of a preferred ribbon which may be used to prepare the ceramic substrate of Figure 1;

Figure 6A is a schematic representation of another preferred ribbon which may be used to prepare the ceramic substrate of Figure 1;

Each of Figures 7 and 8 is schematic of a preferred decal which may be used to prepare the ceramic substrate of Figure 1; and

Each of Figures 9, 10, 10A, and 11 is a flow diagram illustrating how the ribbon, a first decal, a second decal, and the printed ceramic substrate of the invention, respectively, is made.

Description of the preferred embodiments

[0009] Figure 1 is a schematic representation of a printed ceramic substrate 10. Printed ceramic substrate 10 is comprised of a ceramic substrate 12 onto which the color image(s) is fixed.

[0010] The ceramic substrate used in the process of this invention preferentially has a melting temperature of at least 550 degrees Centigrade. The term melting temperature refers to the temperature or range of temperatures at which heterogeneous mixtures, such as a glass batch, glazes, and porcelain enamels, become molten or softened. In one embodiment, it is preferred that the substrate have a melting temperature of at least about 580 degrees Centigrade. In another embodiment, such melting temperature is from about 580 to about 1,200 degrees Centigrade.

[0011] The ceramic substrate used in the process of this invention preferably is a material which is subjected to a temperature of at least about 540 degrees Celsius during processing and is comprised of one or more metal oxides. Typical of such preferred ceramic substrates are, e.g., glass, ceramic whitewares, enamels, porcelains, etc. Thus, e.g., one may use the process of this invention to transfer and fix color images onto ceramic substrates such as dinnerware, outdoor signage, glassware, decorative giftware, architectural tiles, color filter arrays, floor tiles, wall tiles, perfume bottles, wine bottles, beverage containers, and the like.

[0012] Referring again to Figure 1, and in embodiment depicted therein, a flux underlayer 14 is disposed on top of and bonded to the top surface of the ceramic substrate 12. Flux underlayer 14 is preferably transferred to the ceramic substrate surface at a coating weight (coverage) of at least about 1 gram per square meter. It is preferred to use a coating weight (coverage) for flux layer 14 of at least 7 grams per square meter; and it is more preferred to use a coating weight (coverage) for layer 14 of at least about 14 grams per square meter. The coating weight (coverage) referred to herein is a dry weight, by weight of components which contain less than 1 percent of solvent.

[0013] The coating composition used to apply layer 14 onto ceramic substrate 12 must contain frit with a melting temperature of at least about 550 degrees Centigrade. Frit refers to a glass which has been melted and quenched in water or air to form small friable particles which then are processed for milling for use as the major constituent of porcelain enamels, fritted glazes, frit chinaware, and the like.

[0014] In one embodiment, the frit used in the process of this invention has a melting temperature of at least about 750 degrees Centigrade. In another embodiment, the frit used in the process of this invention has a melting temperature of at least about 950 degrees Centigrade.

[0015] One may use commercially available frits. Thus, e.g., one may use a frit sold by the Johnson Matthey Ceramics Inc. (498 Acorn Lane, Downingtown, Pa. 19335) as product number 94C1001 ("Onglaze Unleaded Flux"), 23901 ("Unleaded Glass Enamel Flux,"), and the like. One may use a flux sold by the Cerdec Corporation of P.O. Box 519, Washington, Pa.. 15301 as product number 9630.

[0016] The melting temperature of the frit used should be either substantially the same as or no more than 50 degrees lower than the melting point of the substrate to which the colored image is to be affixed.

[0017] The frit used in the coating composition, before it is melted onto the substrate by the heat treatment process, preferably has a particle size distribution such that substantially all of the particles are smaller than about 10 microns. In one embodiment, at least about 80 weight percent of the particles are smaller than 5.0 microns.

[0018] One may use many of the frits known to those skilled in the art such as, e.g., those described in United States patents 5,562,748, 5,476,894, 5,132,165, 3,956,558, 3,898,362, and the like.

[0019] Referring again to Figure 1, the flux underlayer 14 preferably is comprised of at least about 25 weight percent of one or more frits, by total dry weight of all components in layer 14. In one embodiment, from about 35 to about 85 weight percent of frit material is used in flux underlayer 14. In another embodiment, from about 65 to about 75 percent of such frit material is used.

[0020] It is preferred that the frit material used in layer 14 comprise at least about 5 weight percent, by dry

weight, of silica. The preferred frits used in the process of this invention comprise at least about 98 weight percent of one or more metal oxides selected from the group consisting of lithium, sodium, potassium, calcium, magnesium, strontium, barium, zinc, boron, aluminum, silicon, zirconium, lead, cadmium, titanium, and the like.

[0021] In addition to the frit, layer 14 also is comprised of one or more thermoplastic binder materials in a concentration of from about 0 to about 75 percent, based upon the dry weight of frit and binder in such layer 14. In one embodiment, the binder is present in a concentration of from about 15 to about 35 percent. In another embodiment, the layer 14 is comprised of from about 15 to about 75 weight percent of binder.

[0022] One may use any of the thermal transfer binders known to those skilled in the art. Thus, e.g., one may use one or more of the thermal transfer binders disclosed in United States patent 6,127,316, 6,124,239, 6,114,088, 6,113,725, 6,083,610, 6,031,556, 6,031,021, 6,013,409, 6,008,157, 5,985,076, and the like.

[0023] By way of further illustration, one may use a binder which preferably has a softening point from about 45 to about 150 degrees Celsius and a multiplicity of polar moieties such as, e.g., carboxyl groups, hydroxyl groups, chloride groups, carboxylic acid groups, urethane groups, amide groups, amine groups, urea, epoxy resins, and the like. Some suitable binders within this class of binders include polyester resins, bisphenol-A polyesters, polyvinyl chloride, copolymers made from terephthalic acid, polymethyl methacrylate, vinylchloride/vinylacetate resins, epoxy resins, nylon resins, urethane-formaldehyde resins, polyurethane, mixtures thereof, and the like.

[0024] In one embodiment a mixture of two synthetic resins is used. Thus, e.g., one may use a mixture comprising from about 40 to about 60 weight percent of polymethyl methacrylate and from about 40 to about 60 weight percent of vinylchloride/vinylacetate resin.

[0025] In one embodiment, the binder is comprised of polybutylmethacrylate and polymethylmethacrylate, comprising from 10 to 30 percent of polybutylmethacrylate and from 50 to 80 percent of the polymethylacrylate. In one embodiment, this binder also is comprised of cellulose acetate propionate, ethylenevinylacetate, vinyl chloride/vinyl acetate, urethanes, etc.

[0026] One may obtain these binders from many different commercial sources. Thus, e.g., some of them may be purchased from Dianal America of 9675 Bayport Blvd., Pasadena, Texas 77507; suitable binders available from this source include "Dianal BR 113" and "Dianal BR 106." Similarly, suitable binders may also be obtained from the Eastman Chemicals Company (Box 511, Kingsport, Tennessee).

[0027] Referring again to Figure 1, in addition to the frit and the binder, the layer 14 may optionally contain from about 0 to about 75 weight of wax and, preferably, 5 to about 20 percent of such wax. In one embodiment,

layer 14 is comprised of from about 5 to about 10 weight percent of such wax. Suitable waxes which may be used include caruaba wax, rice wax, beeswax, candelilla wax, montan wax, paraffin wax, microcrystalline waxes, synthetic waxes such as oxidized wax, ester wax, low molecular weight polyethylene wax, Fischer-Tropsch wax, and the like. These and other waxes are well known to those skilled in the art and are described, e.g., in United States patent 5,776,280. One may also use ethoxylated high molecular weight alcohols, long chain high molecular weight linear alcohols, copolymers of alpha olefin and maleic anhydride, polyethylene, polypolyene,

**[0028]** These and other suitable waxes are commercially available from, e.g., the Baker-Hughes Baker Petrolite Company of 12645 West Airport Blvd., Sugarland, Texas.

**[0029]** In one preferred embodiment, caruaba wax is used as the wax. As is known to those skilled in the art, caruaba wax is a hard, high-melting lustrous wax which is composed largely of ceryl palmitate; see, e.g., pages 151-152 of George S. Brady et al's "Material's Handbook," Thirteenth Edition (McGraw-Hill Inc., New York, New York, 1991). Reference also may be had, e.g., to United States patents 6,024,950, 5,891,476, 5,665,462, 5,569,347, 5,536,627, 5,389,129, 4,873,078, 4,536,218, 4,497,851, 4,4610,490, and the like. The entire disclosure of each of these United States patents is hereby incorporated by reference into this specification.

**[0030]** Layer 14 may also be comprised of from about 0 to 16 weight percent of plasticizers adapted to plasticize the resin used. Those skilled in the art are aware of which plasticizers are suitable for softening any particular resin. In one embodiment, there is used from about 1 to about 15 weight percent, by dry weight, of a plasticizing agent. Thus, by way of illustration and not limitation, one may use one or more of the plasticizers disclosed in United States patent 5,776,280 including, e.g., adipic acid esters, phthalic acid esters, chlorinated biphenyls, citrates, epoxides, glycerols, glycol, hydrocarbons, chlorinated hydrocarbons, phosphates, esters of phthalic acid such as, e.g., di-2-ethylhexylphthalate, phthalic acid esters, polyethylene glycols, esters of citric acid, epoxides, adipic acid esters, and the like.

**[0031]** In one embodiment, layer 14 is comprised of from about 6 to about 12 weight percent of the plasticizer which, in one embodiment, is dioctyl phthalate. The use of this plasticizing agent is well known and is described, e.g., in United States patents 6,121,356, 6,117,572, 6,086,700, 6,060,214, 6,051,171, 6,051,097, 6,045,646, and the like.

**[0032]** Referring again to Figure 1, disposed over flux layer 14, is optional opacification layer 16. Opacification layer 16 is optional; but, when it is used, it is preferably used at a coating weight (coverage) of from about 0.5 to about 10 grams per square meter and, more preferably, from about 1 to about 5 grams per square meter.

**[0033]** The opacification layer functions to introduce

whiteness or opacity into the substrate by utilizing a substance that disperses in the coating as discrete particles which scatter and reflect some of the incident light. In one embodiment, the opacifying agent is used on a transparent ceramic substrate (such as glass) to improve image contrast properties.

**[0034]** One may use opacifying agents which were known to work with ceramic substrates. Thus, e.g., one may use one or more of the agents disclosed in United States patents 6,022,819, 4,977,013 (titanium dioxide), 4,895,516 (zirconium, tin oxide, and titanium dioxide), 3,899,346, and the like.

**[0035]** One may obtain opacifying agents obtained from, e.g., Johnson Matthey Ceramic Inc., supra, as, e.g., "Superpax Zirconium Opacifier."

**[0036]** The opacification agent used should have a melting temperature at least about 500 degrees Centigrade higher than the melting point of the frit(s) used in layer 14. Generally, the opacification agent(s) have a melting temperature of at least about 1200 degrees Centigrade. The opacification agent should preferably have a refractive index of greater than 2.0 and, preferably, greater than 2.4.

**[0037]** The opacification agent preferably has a particle size distribution such that substantially all of the particles are smaller than about 10 microns. In one embodiment, at least about 80 weight percent of the particles are smaller than 5.0 microns.

**[0038]** Referring again to Figure 1, in addition to the opacification agent, opacification layer 16 also is comprised of one or more thermoplastic binder materials in a concentration of from about 0 to about 75 percent, based upon the dry weight of opacification agent and binder in such layer 14. In one embodiment, the binder is present in a concentration of from about 15 to about 35 percent. One may use one or more of the binders described with reference to layer 14. Alternatively, one may use one or more other suitable binders.

**[0039]** In addition to the opacifying agent and the optional binder, one may also utilize the types and amounts of wax that are described with reference to layer 14, and/or different amounts of different waxes. Alternatively, or additionally, one may also use the types and amounts of plasticizer described with reference to layer 14. In general, the only substantive differences between layers 14 and 16 are that the calculations are made with respect to the amount of opacifying agent (in layer 16) and not the amount of frit (as is done in layer 14).

**[0040]** Referring again to Figure 1, one may optionally use a second flux layer 18 similar in composition and/or concentrations to layer 14. When such a second flux layer is used, it will be disposed over and printed over the opacification layer 16.

**[0041]** Disposed over the flux layer 14 is one or more color images 20. These ceramic colorant image(s) 20 will be disposed over either the ceramic substrate 12 or the flux layer 14, and/or the optional opacification layer 16 when used, and/or the optional second flux layer 18

when used.

[0042] It is preferred to apply these color image(s) with a digital thermal transfer printer. Such printers are well known to those skilled in the art and are described in International Publication No. WO 97/00781, published on January 7, 1997. As is disclosed in this publication, a thermal transfer printer is a machine which creates an image by melting ink from a film ribbon and transferring it at selective locations onto a receiving material.

[0043] Alternatively, one may use one or more of the thermal transfer printers disclosed in United States patents 6,124,944, 6,118,467, 6,116,709, 6,103,389, 6,102,534, 6,084,623, 6,083,872, 6,082,912, 6,078,346, and the like.

[0044] Digital thermal transfer printers are readily commercially available. Thus, e.g., one may use a printer identified as Gerber Scientific's Edge 2 sold by the Gerber Scientific Corporation of Connecticut. With such a printer, the digital color image(s) may be applied by one or more appropriate ribbon(s).

[0045] Referring again to Figure 1, the colorant, or colorants which form image 20 are mixed with one or more of the ingredients listed for the opacification layer, with the exception that the colorant(s) is substituted for the opacifying agent(s). Thus, a mixture of the colorant and/or binder and/or wax and/or plasticizer may be used. No glass frit is used in colorant image 20.

[0046] It is this element 20 which is selectively applied by the color printer. One such mixture, comprised of one color, may first be digitally printed, optionally followed by one or more differently colored mixtures. The number of colors one wishes to obtain in element 20 will dictate how many different colors are printed.

[0047] The amount of colorant used in the composite 11 should not exceed a certain percentage of the total amount of flux used in such composite, generally being 33.33 percent or less. Put another way, the ratio of the total amount of flux in the composite 11 (which includes layers 14, 18, and 24) to the amount of colorant in element 20, in grams/grams, dry weight, should be at least about 2 and, preferably, should be at least about 3. In one embodiment, such ratio is at least 4.0. In another such embodiment, such ratio of flux/colorant is from about 5 to 6.

[0048] In another embodiment of the invention, the ratio of frit used in the process to colorant used in the process is at least 1.25.

[0049] The unexpected results which obtain when the flux/colorant ratios of this invention are substituted for the flux/colorant ratios of the Tanaka patent, and when the flux and colorant layers are separated, are dramatic. A substantially more durable product is produced by the process of the instant invention.

[0050] The colorants which work well in applicants' process preferably each contain at least one metal-oxide. Thus, a blue colorant can contain the oxides of a cobalt, chromium, aluminum, copper, manganese, zinc,

etc. Thus, e.g., a yellow colorant can contain the oxides of one or more of lead, antimony, zinc, titanium, vanadium, gold, and the like. Thus, e.g., a red colorant can contain the oxides of one or more of chromium, iron (two valence state), zinc, gold, cadmium, selenium, or copper. Thus, e.g., a black colorant can contain the oxides of the metals of copper, chromium, cobalt, iron (plus two valence), nickel, manganese, and the like. Furthermore, in general, one may use colorants comprised of the oxides of calcium, cadmium, zinc, aluminum, silicon, etc.

[0051] Suitable colorants are well known to those skilled in the art. See, e.g., United States patents 6,120,637, 6,108,456, 6,106,910, 6,103,389, 6,083,872, 6,077,594, 6,075,927, 6,057,028, 6,040,269, 6,040,267, 6,031,021, 6,004,718, 5,977,263, 6,086,846, 6,077,797 (a mixture of chromium oxide and blue cobalt spinel), 6,075,223 (oxides of transition elements or compounds of oxides of transition elements), 6,045,859 (pink coloring element), 5,988,968 (chromium oxide, ferric oxide), 5,968,856 (glass coloring oxides such as titania, cesium oxide, ferric oxide, and mixtures thereof), 5,962,152 (green chromium oxides), 5,912,064, 5,897,885, 5,895,511, 5,820,991 (coloring agents for ceramic paint), 5,702,520 (a mixture of metal oxides adjusted to achieve a particular color), and the like.

[0052] The ribbons produced by the process of this invention are preferably leach-proof and will not leach toxic metal oxide.

[0053] The particle size distribution of the colorant used in layer 20 should preferably be within a relatively narrow range. It is preferred that the colorant have a particle size distribution such that at least about 90 weight percent of its particles are within the range of 0.2 to 20 microns.

[0054] The colorant used preferably has a refractive index greater than 1.4 and, more preferably, greater than 1.6; and, furthermore, the colorant should not decompose and/or react with the molten flux when subjected to a temperature in range of from about 550 to about 1200 degrees Celsius.

[0055] Referring again to Figure 1, a flux layer 22 optionally may be disposed over the ceramic colorant image element 20. Thus flux layer, when used, will be comparable to the flux layer 18 but need not necessarily utilize the same reagents and/or concentrations and/or coating weight.

[0056] Disposed over the colorant image element 20, and coated either onto such element 20 or the optional flux layer 22, is a flux covercoat 24.

[0057] Covercoats are described in the patent art. See, e.g., United States patents 6,123,794 (covercoat used in decal), 6,110,632, 5,912,064, 5,779,784 (Johnson Matthey OPL 164 covercoat composition), 5,779,784, 5,601,675 (screen printed organic covercoat), 5,328,535 (covercoat for decal), 5,229,201, and the like.

[0058] The covercoat 24, in combination with the oth-

er flux-containing layers, must provide sufficient flux so that the ratio of flux to colorant is within the specified range. Furthermore, it must apply structural integrity to the ceramic colorant image element 20 so that, when composite 10 is removed from its backing material, it will retain its structural integrity until it is applied to the ceramic substrate.

[0059] The covercoat 24 should be substantially water-insoluble so that, after it is contacted with water at 40 degrees Centigrade for 1 minute, less than 0.5 percent will dissolve.

[0060] The covercoat 24 should preferably have an elongation before break, as measured by standard A.S. T.M. Test D638-58T, of more than 5 percent.

[0061] The covercoat 24 should be applied at a sufficient coating weight to result in a coating weight of at least 2 grams per square meter and, more preferably, at least 5 grams per square meter.

[0062] The covercoat 24 preferably is comprised of the aforementioned flux and carbonaceous material(s) which, in one preferred embodiment, when subjected to a temperature of 440 degrees Centigrade for at least 5 minutes, will be substantially completely converted to gaseous material. The aforementioned binders, and/or waxes, and/or plasticizers described, e.g., with relation to layers 14, 16, 18, 20, 22, and 24, are suitable carbonaceous materials, and one or more of them may be used in the proportions described with regard to layer 14 to constitute the covercoat.

[0063] One may use a covercoat 24 which is similar in composition and structure to the layer 14. In one embodiment, it is preferred that the covercoat 24 be comprised of a binder selected from the group consisting of polyacrylate binders, polymethacrylate binders, polyacetal binders, mixtures thereof, and the like.

[0064] Some suitable polyacrylate binders include polybutylacrylate, polyethyl-co-butylacrylate, poly-2-ethylhexylacrylate, and the like.

[0065] Some suitable polymethacrylate binders include, e.g., polymethylmethacrylate, polymethylmethacrylate-co-butylacrylate, polybutylmethacrylate, and the like.

[0066] Some suitable polyacetal binders include, e.g., polyvinylacetal, polyvinylbutyral, polyvinylformal, polyvinylacetal-co-butylal, and the like.

[0067] Covercoat 24 preferably should have a softening point in the range of from about 50 to about 150 degrees Centigrade.

[0068] In one embodiment, covercoat 24 is comprised of from 0 to 75 weight percent of frit and from 25 to about 100 weight percent of a material selected from the group consisting of binder, wax, plasticizer and mixtures thereof.

[0069] Figure 2 is a schematic representation of a preferred ribbon which may be used in the process of this invention. Ribbon 30 is comprised of a flexible substrate 32.

[0070] Substrate 32 may be any substrate typically

used in thermal transfer ribbons such as, e.g., the substrates described in United States patent 5,776,280.

[0071] In one embodiment, substrate 32 is a flexible material which comprises a smooth, tissue-type paper such as, e.g., 30-40 gauge capacitor tissue. In another embodiment, substrate 32 is a flexible material consisting essentially of synthetic polymeric material, such as poly(ethylene terephthalate) polyester with a thickness of from about 1.5 to about 15 microns which, preferably, is biaxially oriented. Thus, e.g., one may use polyester film supplied by the Toray Plastics of America (of 50 Belvedere Avenue, North Kingstown, Rhode Island) as catalog number F53.

[0072] By way of further illustration, substrate 32 may be any of the substrate films disclosed in United States patent 5,665,472. Thus, e.g., one may use films of plastic such as polyester, polypropylene, cellophane, polycarbonate, cellulose acetate, polyethylene, polyvinyl chloride, polystyrene, nylon, polyimide, polyvinylidene chloride, polyvinyl alcohol, fluororesin, chlorinated resin, ionomer, paper such as condenser paper and paraffin paper, nonwoven fabric, and laminates of these materials.

[0073] Affixed to the bottom surface of substrate 32 is backcoating layer 34, which is similar in function to the "backside layer" described at columns 2-3 of United States patent 5,665,472. The function of this backcoating layer 34 is to prevent blocking between a thermal backing sheet and a thermal head and, simultaneously, to improve the slip property of the thermal backing sheet.

[0074] Backcoating layer 34, and the other layers which form the ribbons of this invention, may be applied by conventional coating means. Thus, by way of illustration and not limitation, one may use one or more of the coating processes described in United States patents 6,071,585 (spray coating, roller coating, gravure, or application with a kiss roll, air knife, or doctor blade, such as a Meyer rod), 5,981,058 (myer rod coating), 5,997,227, 5,965,244, 5,891,294, 5,716,717, 5,672,428, 5,573,693, 4,304,700, and the like.

[0075] Thus, e.g., backcoating layer 34 may be formed by dissolving or dispersing the above binder resin containing additive (such as a slip agent, surfactant, inorganic particles, organic particles, etc.) in a suitable solvent to prepare a coating liquid. Coating the coating liquid by means of conventional coating devices (such as Gravure coater or a wire bar) may then occur, after which the coating may be dried.

[0076] One may form a backcoating layer 34 of a binder resin with additives such as, e.g., a slip agent, a surfactant, inorganic particles, organic particles, etc.

[0077] Binder resins usable in the layer 34 include, e.g., cellulosic resins such as ethyl cellulose, hydroxyethylcellulose, hydroxypropylcellulose, methylcellulose, cellulose acetate, cellulose acetate butyrate, and nitrocellulose. Viny resins, such as polyvinylalcohol, polyvinylacetate, polyvinylbutyral, polyvinylacetal, and pol-

yvinylpyrrolidone also may be used. One also may use acrylic resins such as polyacrylamide, polyacrylonitrile-co-styrene, polymethylmethacrylate, and the like. One may also use polyester resins, silicone-modified or fluorine-modified urethane resins, and the like.

[0078] In one embodiment, the binder comprises a cross-linked resin. In this case, a resin having several reactive groups, for example, hydroxyl groups, is used in combination with a crosslinking agent, such as a polyisocyanate.

[0079] In one embodiment, a backcoating layer 34 is prepared and applied at a coat weight of 0.05 grams per square meter. This backcoating 34 preferably is a polydimethylsiloxane-urethane copolymer.

[0080] One may apply backcoating 34 at a coating weight of from about 0.01 to about 2 grams per square meter, with a range of from about 0.02 to about 0.4 grams/square meter being preferred in one embodiment and a range of from about 0.5 to about 1.5 grams per square meter being preferred in another embodiment.

[0081] Referring again to Figure 2, substrate 32 contains an optional release layer 36 coated onto its top surface of the substrate. The release layer 36, when used, facilitates the release of the ceramic colorant/binder layer 38 from substrate 32 when a thermal ribbon 30 is used to print at high temperatures.

[0082] Release layer 36 preferably has a thickness of from about 0.2 to about 2.0 microns and typically is comprised of at least about 50 weight percent of wax. Suitable waxes which may be used include caruaba wax, rice wax, beeswax, candelilla wax, montan wax, paraffin wax, microcrystalline waxes, synthetic waxes such as oxidized wax, ester wax, low molecular weight polyethylene wax, Fischer-Tropsch wax, and the like. These and other waxes are well known to those skilled in the art and are described, e.g., in United States patent 5,776,280.

[0083] In one embodiment, at least about 75 weight percent of layer 36 is comprised of wax. In this embodiment, the wax used is preferably caruaba wax.

[0084] Minor amounts of other materials may be present in layer 36. Thus, one may include from about 5 to about 20 weight percent of heat-softening resin which softens at a temperature of from about 60 to about 150 degrees Centigrade. Some suitable heat-softening resins include, e.g., the heat-meltable resins described in columns 2 and of United States patent 5,525,403. In one embodiment, the heat-meltable resin used is polyethylene-co-vinylacetate with a melt index of from about 40 to about 2500 dg. per minute.

[0085] Referring to Figure 2, the layer 36 may be omitted and the layer 38 may be directly contiguous with substrate 32.

[0086] Ceramic colorant/binder layer 38 is one of the layers used to produce the ceramic colorant image 20. In the process of the invention, a multiplicity of ribbons 30, each one of which preferably contains a ceramic colorant/binder layer 38 with different colorant(s), are dig-

itally printed to produce said ceramic colorant image 20. What these ribbons have in common is that they all contain both binder and colorant material of the general type and in the general ratios described for layer 20. In one preferred embodiment, there is substantially no glass frit in layer 20 (i.e., less than about 5 weight percent). The concentrations of colorant and binder, and the types of colorant and binder, need not be the same for each ribbon. What is the same, however, are the types of components in general and their ratios.

[0087] Figure 3 is a schematic representation of a preferred ribbon 40 which is similar to the ribbon 30 depicted in Figure 2 but differs therefrom in that it utilizes a flux layer 42 instead of the ceramic colorant and binder element 38. The flux layer 42, in general, has similar components, and ratios, as the composition of flux layer 18 (see Figure 1) and is used to deposit layer 14 and/or layer 18 and/or layer 22 onto the ceramic substrate 12. The precise composition and coating weight of flux layer 42 will depend upon the precise composition and coating weight of the flux layer 14 and/or flux layer 18 and/or flux layer 22 desired.

[0088] In the embodiment depicted in Figure 1, at least 4 separate flux-containing layers are depicted. In general, it is preferred to utilize at least two such layers. In general, the number of layers of flux required will depend upon how much total flux must be used to keep the total flux/colorant ratio in composite 11 at least 2.0.

[0089] It is preferred not to dispose all of the flux required in one layer. Furthermore, it is preferred that at least some of the flux be disposed below the ceramic colorant image, and at least some of the flux be disposed above the ceramic colorant image.

[0090] In one embodiment, at least 10 weight percent of the total amount of flux used should be disposed on top of ceramic colorant image 20 in one or more flux layers (such as layers 22 and 24). In this embodiment, at least about 50 percent of the total amount of flux should be disposed below ceramic colorant image 20 in one or more of flux layer 18 and/or flux layer 14.

[0091] In another embodiment, from about 30 to about 70 weight percent of the entire amount of frit used in the process of this invention is disposed below the ceramic image 20, and from about 70 to about 30 weight percent of the entire amount of frit used in the process of the invention should be disposed above the ceramic image 20. A layer of material which contains frit need not necessarily be contiguous with the ceramic colorant image 20 to be disposed either below or above it. Thus, e.g., the flux underlayer 14 is not contiguous with the ceramic colorant image 20 but is still disposed below such image.

[0092] In one embodiment, from about 40 to about 60 weight percent of the entire amount of frit used in the process of this invention is disposed below the ceramic image 20, and from about 60 to about 40 weight percent of the entire amount of frit used in the process of the invention should be disposed above the ceramic image

20. In yet another embodiment, from about 75 to about 90 weight percent of the entire amount of frit used in the process of this invention is disposed below the ceramic image 20, and from about 25 to about 10 weight percent of the entire amount of frit used in the process of the invention should be disposed above the ceramic image 20

[0093] If the required amount of flux is not disposed above the ceramic colorant image 20, applicants have discovered that poor color development occurs when cadmium pigments and other pigments are used.

[0094] For non-cadmium-containing ceramic colorant images, applicants have discovered that acceptable results utilizing a single layer of frit may be obtained so long as the single layer of frit is positioned both above the colorant image 20 and the ceramic substrate 12 and provides a ratio of total frit to ceramic colorant in excess of about 1.25, weight/weight.

[0095] Figure 4 is a schematic of yet another preferred ribbon 50 which is similar in construction to the ribbons depicted in Figures 2 and 3 but differs therefrom in containing a different arrangement of layers.

[0096] Figure 5 is a schematic of yet another preferred ribbon 52 which is similar to the ribbons depicted in Figures 2, 3, and 4 but differs therefrom in containing a flux covercoat layer 46. The flux covercoat layer 46 may be used to deposit the flux covercoat 24 (see Figure 1) and, thus, should have a composition similar to the desired covercoat 24.

[0097] Figure 6 is a schematic of yet another preferred ribbon 54 which is similar to the other ribbons depicted but which, additionally, is comprised of opacification layer 48. The opacification layer 48 may be used to print opacification layer 16 (see Figure 1) and, thus, should contain substantially the same components and ratios as described for layer 16.

[0098] Figure 6A is a schematic representation of a another preferred ribbon 60 of the invention which is comprised of backcoating layer 34, polyester support 32, and release layer 36. Disposed on top of release layer 36 are a multiplicity of panels which are disposed at selected locations on top of release layer 36. Using conventional printing techniques, one of such panels (such as panel 42) is first coated onto release layer 36 at the desired location, followed by selective coating of the second panel 48, the third panel 38 etc.

[0099] To obtain such selective location(s) of the panels, one may a gravure coating press. What is obtained with this process is a ribbon with repeating sequences of various panels, which thus can be utilized in a single head thermal transfer printer to obtain a print image with multiple colors and or compositions and/or properties.

[0100] In this embodiment, it is preferred to use a sequence of 42/48/38/38/38/46 to obtain, with printing operation, a covercoated decal which may be used to produce an image on a ceramic substrate with good print density and good durability.

[0101] Figure 7 is a schematic representation of a ce-

ramic decal 70, which can be produced using one or more of the ribbons depicted in Figures 2 through 6A. The various panels 38 shown in Figure 6A represent one or more ceramic colorant panels used to produce a ceramic colorant image 20.

[0102] Referring to Figure 7, and in the preferred embodiment depicted therein, the ceramic decal 70 is preferably comprised of flexible substrate 72.

[0103] Flexible substrate 72 is often referred to as a "backing sheet" in the prior art; see, e.g., United States patent 5,132,165. Thus, e.g., substrate 72 can include a dry strippable backing or a solvent mount or a water mount slide-off decal. The backing may be of paper or other suitable material such as, e.g., plastic, fabric, and the like. In one embodiment, the backing comprises paper which is coated with a release material, such as dextrine-coated paper. Other possible backing layers include those coated with polyethylene glycol and primary aliphatic oxyethylated alcohols.

[0104] By way of further illustration, one may use "Waterslide" paper, which is commercially available paper with a soluble gel coat; such paper may be obtained from Brittiens Papers Company of England. This paper is also described in United States patents 6,110,632, 5,830,529, 5,779,784, and the like.

[0105] Additionally, one may use heat transfer paper, i.e., commercially available paper with a wax coating possessing a melt point in the range of from about 65 to about 85 degrees Centigrade. Such heat transfer paper is discussed, e.g., in United States patents 6,126,669, 6,123,794, 6,025,860, 5,944,931, 5,916,399, 5,824,395, 5,032,449, and the like.

[0106] Regardless of what paper is used, it is optionally preferred that a flux layer 74 be either coated to or printed on such paper 72. The thickness of such coating 74 should be at least about 5 microns after such coating has dried, and even more preferably at least about 7 microns.

[0107] Referring again to Figure 7, ceramic colorant images 76 (yellow), and/or 78 (magenta) and/or 80 (cyan) and/or 82 (black) may be digitally printed by sequentially using one or more ribbons 30. Flux layers 42 may optionally be printed by utilizing ribbon 40, which can sequentially print layer 42 in between the various image colors. Alternatively, layer 42 may be printed simultaneously with the image colors by the use of ribbon 50.

[0108] Figure 8 is a schematic representation of a decal 80 which is similar in many respects to decal 70 (see Figure 7) but differs therefrom in containing an opacification layer 48 which is similar in function and composition to the opacification layer 48 depicted for ribbon 54 (see Figure 6); in another embodiment, not shown, the flux underlayer 14 is omitted. In image 20, a multiplicity of ceramic images may be digitally printed and superimposed on each other to form such image.

[0109] Figure 9 is a flow diagram of one preferred process for preparing a ribbon of this invention. The process illustrated may be used to prepare ribbon 30,



and/or ribbon 40, and/or ribbon 50, etc.

**[0110]** In step 100, one may prepare a ceramic colorant ink in accordance with the description, e.g., of layer 38 of Figure 2. This ink may be used to coat the faceside of polyester support 32 in step 114 (see Figure 2).

**[0111]** In step 102, one may prepare a flux binder ink; see, e.g., layer 42 of Figure 3 and its accompanying description. This flux binder ink may be used to either directly coat the faceside of the polyester support 32 in step 112, and/or coat over an optional release layer 36 in step 110.

**[0112]** In step 104, a release layer is prepared; see, e.g., release layer 36 of Figure 2 and its accompanying description. This release layer 36 may optionally be used in step 110 to coat the face side of the polyester substrate 32.

**[0113]** In step 106, a backcoat ink may be prepared; see, e.g., backcoating layer 34 of Figure 2 and its accompanying description. This backcoat layer 34 may be used to coat the backside of the polyester substrate in step 108.

**[0114]** In step 114, the faceside of the polyester support 32 may be coated with ceramic colorant ink.

**[0115]** Using the combination of steps illustrated in Figure 9, one may readily prepare one or more of the ribbons illustrated in Figures 2 through 5. Furthermore, although not specifically depicted in Figure 9, one may prepare an opacification layer in accordance with the description of opacification layer 48 (See Figure 6 and its accompanying description) which may be used to prepare ribbons containing such opacification layer; also see Figure 6A).

**[0116]** Figure 10 is a schematic diagram of a preferred process for producing a ceramic decal. In step 120, either heat transfer or Waterslide paper is provided; these papers are described in the specification (see element 72 of Figure 7 and its accompanying description). A flux and binder layer is either coated or printed on the face of such optional step 122 (see element 74 of Figure 7 and its accompanying description); and this flux and binder layer, when dried, should be at least about 7 microns thick.

**[0117]** In step 124, one may optionally print an opacification layer onto the flux binder layer described in step 122. This opacification layer corresponds to layer 48 of Figure 8. It is preferred, when such opacification layer is used in step 122, to print an optional flux/binder layer over the opacification layer in step 126; this optional flux binder layer is described as element 42 of Figure 8. However, the optional flux/binder layer may be omitted, and one may proceed directly from step 124 to step 128. Alternatively, one may omit both the opacification step and the optional flux binder layer step and proceed directly from step 122 to 128. It is preferred to use a ceramic colorant thermal transfer ribbon 114 in step 128.

**[0118]** In step 128, which may optionally be repeated one or more times with different ceramic colorant ribbons 114, a color image is digitally printed using such

ribbon 114 and a digital thermal transfer printer. In one embodiment, prints were produced using a Zebra 140XiII thermal transfer printer run at 4 inches per second with energy level settings ranging from 18 to 24.

**[0119]** The digital image to be printed is composed of one or more primary colors, and such image is evaluated to determine how many printings of one or more ceramic colorants are required to produce the desired image. Thus, in decision step 130, if another printing of the same or a different colored image is required, step 128 is repeated. If no such additional printing is required, one may then proceed to step 132 and/or step 134.

**[0120]** In optional step 132, an optional flux binder layer is printed over the ceramic colorant image produced in step(s) 128. This optional flux binder layer corresponds to element 42 of Figure 8. Thereafter, either one goes from step 132 to 134, or one goes directly from decision step 130 to step 134. In printing step 134, a flux covercoat corresponding to element 24 of Figure 8 is printed to complete the decal. One may apply the covercoat over the entire decal (which includes both a printed image and unprinted area(s)). Alternatively, one may apply the covercoat over the entire imaged areas.

**[0121]** Thus, a complete decal is produced in Figure 10 and now may be used in Figure 11 to produce the imaged ceramic article.

**[0122]** Figure 10A illustrates an alternative process for preparing a decal according to the invention. The process illustrated in Figure 10A is very similar to the process illustrated in Figure 10 with several exceptions. In the first place, in the process of Figure 10A, in step 150 the covercoat is applied or printed to the assembly prior to the time the ceramic colorant image 128 is applied. Thereafter, following the application of ceramic colorant image 128, optional flux binder (step 126), and/or opacifying agent (step 124), and/or flux/binder (step 122) may be applied to form the decal 152.

**[0123]** In the process depicted in Figure 11, the decal produced in step 134 of Figure 10 is treated in one of two ways, depending upon whether the substrate comprising the decal is Waterslide or heat transfer paper.

**[0124]** If the substrate comprising the image is Waterslide paper, then the decal is first soaked in hot water (at a temperature of greater than 40 degrees Centigrade, for preferably at least about 30 seconds). In step 138, the image on the Waterslide paper is then separated from the paper in step 140, this image is then placed onto a ceramic substrate and smoothed to remove wrinkles or air bubbles in step 142 and dried; and the image is then "fired." The imaged ceramic substrate is subjected to a temperature of from about 550 to about 1200 degrees Centigrade in step 144.

**[0125]** If, alternatively, the substrate is heat transfer paper, then the decal is heated above the melting point of the wax release layer on the paper in step 146; such temperature is generally from about 50 to about 150 degrees Centigrade. Thereafter, while said wax release layer is still in its molten state, one may remove the ce-

ramic colorant image from the paper in step 148, position the image onto the ceramic article in step 150, and then follow steps 142 and 144 as described hereinabove.

[0126] The following Examples are presented to illustrate the claimed invention but are not to be deemed limitative thereof. Unless otherwise specified, all parts are by weight and all temperatures are in degrees Centigrade.

#### Example 1

[0127] In this example, three different flexible substrate elements were prepared in order to print a decal. The first such flexible substrate element was a coated waterslide paper. The second flexible substrate element contained colored oxide material. The third such flexible substrate element contained frit. The latter two flexible substrate elements were used to print a decal onto the coated waterslide paper.

[0128] A colored oxide flexible substrate element was prepared. A 4.5 micron thick poly (ethylene terephthalate) film was used as a substrate film, and it was backcoated with a polydimethylsiloxane-urethane copolymer at a coat weight of 0.03 grams per square meter. The copolymer composition was applied with a Myer Rod and dried in an oven, at a temperature of 50 degrees Centigrade for 15 seconds.

[0129] A release coating composition was prepared for application to the face coat of the polyester film. To a mixture of 38 grams of reagent grade toluene and 57 grams of reagent grade isopropyl alcohol were charged 0.58 grams of Diacarna 3B (an alpha-olefin sold by the Mitsubishi Kasai Company of Japan), 0.6 grams of EV-ALEX V577 (an ethylene-vinylacetate resin sold by the DuPont Mitsui and Polychemicals Company of Japan), and 3.82 grams of "POLYWAX 850" (a polyethylene wax sold by the Baker Hughes Baker Petrolite Company of Sugarland Texas). This mixture was stirred until the components were fully dissolved. Then it was coated with a Myer Rod at a coating weight of 0.5 grams per square meter and thereafter dried for 15 seconds at 50 degrees Centigrade.

[0130] The polyester film, with its backcoating and release coating, then was coated with a colored oxide layer at a coating weight of 3.2 grams per square meter; the colored oxide layer was applied to the release layer. The color coating was prepared by mixing 45.02 grams of hot toluene (at a temperature of 60 degrees Centigrade) with 13.51 grams of a mixture of Dianal BR 106 and Dianal BR 113 binders in weight/weight ratio of 1/3; these binders were purchased from the Dianal America Company of Pasadena, Texas. Thereafter, 25 grams of Chrome Blue pigment (sold by Johnson Matthey Ceramic Inc. of Downingtown, Pa.) were charged to the mixture. The composition thus produced was mixed with 35 grams of ceramic grinding media and milled on a paint shaker for 15 minutes until substantially all of the parti-

cles were smaller than 10 microns. Thereafter, 3.57 grams of Unilin 425 (a wax sold by the Baker Hughes Baker Petrolite Company) were dissolved in sufficient reagent grade methylethylketone to prepare a 15 percent solution, and this wax solution was then charged to the mixture with stirring, until a homogeneous mixture was obtained. Thereafter the mixture was filtered to separate the filtrate from the grinding media, and the filtrate was then coated onto the release layer of the polyester substrate at a coating weight of 3.2 grams per square meter using a Meyer Rod. The coated substrate thus produced was then dried with a hot air gun.

[0131] A polyester film with a backcoat and a release coat was prepared in the manner described above, but a frit covercoat layer was coated over the release coat instead of the colored oxide layer. This frit covercoat layer was prepared by mixing 42.05 grams of isopropyl alcohol and 42.05 grams of methylethylketone. This solvent mixture was heated to a temperature of 50 degrees Centigrade, and to this hot solvent mixture were charged 11.36 grams of "BUTVAR 79" (a polyvinylbutyral resin sold by the American Cyanamid Company) and 1.26 grams of cellulose acetate butyrate (CAB 553.04, sold by the Eastman Chemical Company of Kingsport, Tenn.), with mixing. The mixture was then allowed to cool to ambient temperature, and then 3.28 grams of dioctylphthalate were added with mixing. Thereafter 45.36 grams of a frit (sold by the Cerdec Corporation of Washington, Pa. as "product number 9630") were charged to the mixture and mixed. Grinding media was then added to the mixture, and the mixture then was comminuted by shaking it on a paint mixer for 15 minutes until substantially all of its particles were smaller than about 10 microns. Thereafter, the filtrate was separated from the grinding media by filtration, and the filtrate was then coated at a coating weight of 7.0 grams per square meter onto the release coat of the coated polyester film. The coated film was then dried for 15 seconds with an air gun.

[0132] A coated waterslide paper was prepared. The waterslide paper was obtained from the Brittain's Papers Company of England, and an overcoat composition was prepared to coat onto the gel side of this paper.

[0133] To prepare the overcoat composition, 38.5 grams of methylethylketone and 38.5 grams of isopropyl alcohol were mixed and then heated to a temperature of 60 degrees Centigrade. To this warm solvent mixture were added 10.4 grams of polyvinylbutyral resin (sold as BUTVAR 79 by the American Cyanamid Company) and 1.14 grams of cellulose acetate butyrate (CAB 553.04, Eastman Chemical) with stirring, to prepare a substantially homogeneous solution. Thereafter, 11.44 grams of a frit sold by the Cerdec Corporation of Post Office Box 519, Washington, Pa. as "product number 9630" were added to the mixture, with stirring; this frit is comprised of sodium borosilicate. frit. The mixture was then mixed for about 10 minutes, until it was substantially homogeneous.

[0134] Ceramic grinding media were added to the mixture, and the media and mixture were then shaken on a paint mixer for 16 minutes until the maximum particle size of the particles in the mixture was less than 10 microns. Thereafter, the grinding media were removed from the comminuted mixture by filtration.

[0135] The comminuted filtrate was then coated onto the gel face of the waterslide paper at a coating weight (coverage) of 14 grams per square meter. The coated substrate was then allowed to dry under ambient conditions for eight hours.

[0136] Printing was conducted using a Zebra 140X thermal transfer printer. The prints were created at 4 inches per second and at energy levels ranging from 18 to 24. Printing was done directly onto the overcoat of the waterslide paper. A digital color image was first printed using the colored oxide ribbon described in this example, and then a covercoat layer was printed over the digital image by printing with the frit covercoat ribbon of this example.

[0137] The printed waterslide paper was then immersed in warm (40 degree Centigrade) water for 30 seconds. The decal was then separated from the paper backing, and the decal so separated was then positioned onto a porcelain-coated steel substrate and smoothed to remove bubbles and wrinkles using a squeegee. The porcelain-coated steel substrate was purchased from High Standard, Inc. of Dublin, New Hampshire.

[0138] The decal/substrate assembly was then allowed to dry under ambient conditions for 8 hours. It was then fired by heating it for 10 minutes at a temperature of 454 degrees Centigrade, then increasing the temperature to 690 degrees Centigrade and holding it at this temperature for ten minutes, and then allowing the heated assembly to slowly cool to ambient.

[0139] The image on the porcelain-coated steel had excellent color density with good image definition. It also was resistant to abrasion.

#### Example 2

[0140] The procedure of Example 1 was substantially repeated with the exception that a red cadmium oxide powder (Cadmium Red pigment, obtained from Johnson Matthey) was used instead of the Chrome Blue pigment of Example 1. The image on the porcelain-coated steel had excellent color density with good image definition, and it was also resistant to abrasion.

#### Example 3

[0141] The procedure of Example 1 was substantially repeated with the exception that a black oxide powder (Chrome Black 1795, obtained from Johnson Matthey) was used instead of the Chrome Blue pigment of Example 1. The image on the porcelain-coated steel had excellent color density with good image definition, and it

was also resistant to abrasion.

[0142] It is to be understood that the aforementioned description is illustrative only and that changes can be made in the apparatus, in the ingredients and their proportions, and in the sequence of combinations and process steps, as well as in other aspects of the invention discussed herein, without departing from the scope of the invention as defined in the following claims.

#### **Claims**

1. A process for preparing a ceramic decal, comprising the steps of sequentially:

(a) preparing a first printed image substrate, by a process comprising the steps of applying to a backing sheet a digitally printed ceramic colorant image comprised of a colorant composition, wherein:

1. said colorant composition is comprised of metal oxide pigment with a refractive index greater than about 1.4,
2. said colorant composition is comprised of a multiplicity of metal oxide pigment particles, at least about 90 weight percent of which are within the range of about 0.2 to about 20 microns,
3. said colorant composition is comprised of a first solid carbonaceous binder, and
4. said digitally printed ceramic colorant image comprises a first surface,

(b) digitally printing to said first surface of said first printed ceramic colorant image a flux covercoat comprised of a first mixture comprised of a first frit and a second solid carbonaceous binder, wherein:

1. said first frit has a melting temperature of at least about 550 degrees Centigrade,
2. said flux covercoat is printed over at least all of said first surface of said digitally printed ceramic colorant image, and
3. the total amount of frit applied to said backing sheet is at least 2 times as great as the total amount of colorant applied to said backing sheet.

2. The process as recited in claim 1, further comprising the step of preparing said backing sheet by a process comprising the steps of applying to a backing sheet a second mixture comprised of a second frit and a third solid carbonaceous binder, wherein said second frit has a melting temperature of at least about 550 degrees Centigrade.

3. The process as recited in claim 2, wherein:

(a) said second mixture is applied to said backing sheet at coverage of at least about 10 grams per square meter,

(b) said second frit comprises at least about 25 weight percent of said second mixture of said second frit and said third solid carbonaceous binder binder,

(c) said flux covercoat is applied to said first printed ceramic colorant image at coverage of at least 2 grams per square meter,

(d) said flux covercoat is comprised of at least about 25 weight percent of said second frit,

provided that the total amount of frit applied to said backing sheet is at least about 4 times as great as the total amount of colorant applied to said backing sheet.

4. The process as recited in claim 2, further comprising the step of printing an opacifying agent over said backing sheet prior to the time said digitally printed ceramic colorant image is applied to said backing sheet.

5. The process as recited in claim 4, wherein said opacifying agent has a refractive index greater than 2.0.

6. The process as recited in claim 5, further comprising the step of printing a third mixture of a third frit and a fourth solid carbonaceous binder binder over said opacifying agent prior to the time said digitally printed ceramic colorant image is applied to said backing sheet.

7. A process for preparing a ceramic decal, comprising the steps of sequentially:

(a) applying to a backing sheet a flux covercoat with a first surface comprised of a first mixture comprised of a first frit and a second solid carbonaceous binder, wherein said first frit has a melting temperature of at least about 550 degrees Centigrade,

(b) applying to said first surface of said flux covercoat a a digitally printed ceramic colorant image comprised of a colorant composition comprising a second surface, wherein:

1. said colorant composition is comprised of metal oxide pigment with a refractive index greater than about 1.4,

2. said colorant composition is comprised of a multiplicity of metal oxide pigment particles, at least about 90 weight percent of which are within the range of about 0.2 to

about 20 microns, and

3. said colorant composition is comprised of a first solid carbonaceous binder,

4. said second surface of said colorant composition is contiguous with at least a portion of said first surface of said flux covercoat, and

5. the total amount of frit applied to said backing sheet is at least 2 times as great as the total amount of colorant applied to said backing sheet.

8. The process as recited in claim 7, further comprising the step of overprinting said second surface of said ceramic colorant image by a process comprising the steps of applying to said ceramic colorant image a second mixture comprised of a second frit and a third solid carbonaceous binder, wherein said second frit has a melting temperature of at least about 550 degrees Centigrade.

9. The process as recited in claim 25, wherein:

(a) said second mixture is applied to said ceramic colorant image at a coverage of at least about 10 grams per square meter,

(b) said second frit comprises at least about 25 weight percent of said second mixture of said second frit and said third solid carbonaceous binder binder,

(c) said flux covercoat is applied to said backing sheet at a coverage of at least 2 grams per square meter,

(d) said flux covercoat is comprised of at least about 25 weight percent of said first frit,

provided that the total amount of frit applied to said backing sheet is at least about 4 times as great as the total amount of colorant applied to said backing sheet.

10. The process as recited in claim 9, wherein each of said first carbonaceous binder, said second carbonaceous binder, and said third carbonaceous binder is comprised of less than about 15 weight percent of liquid.

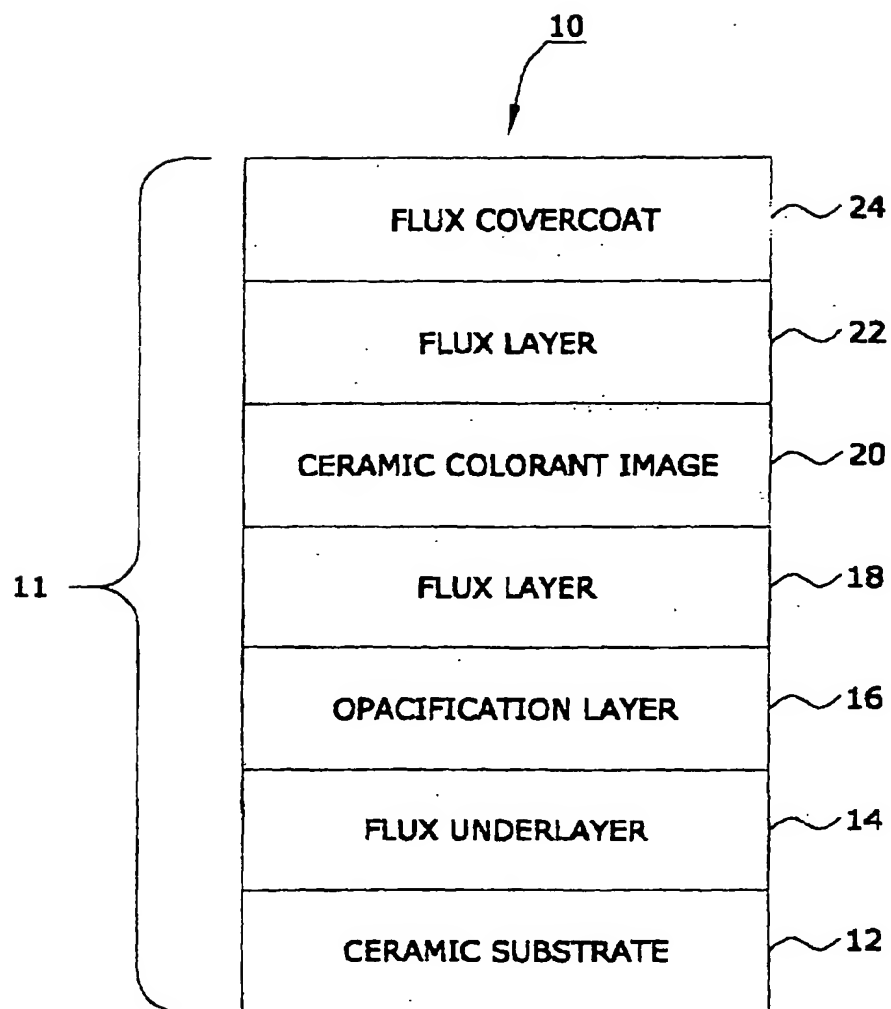


FIG. 1

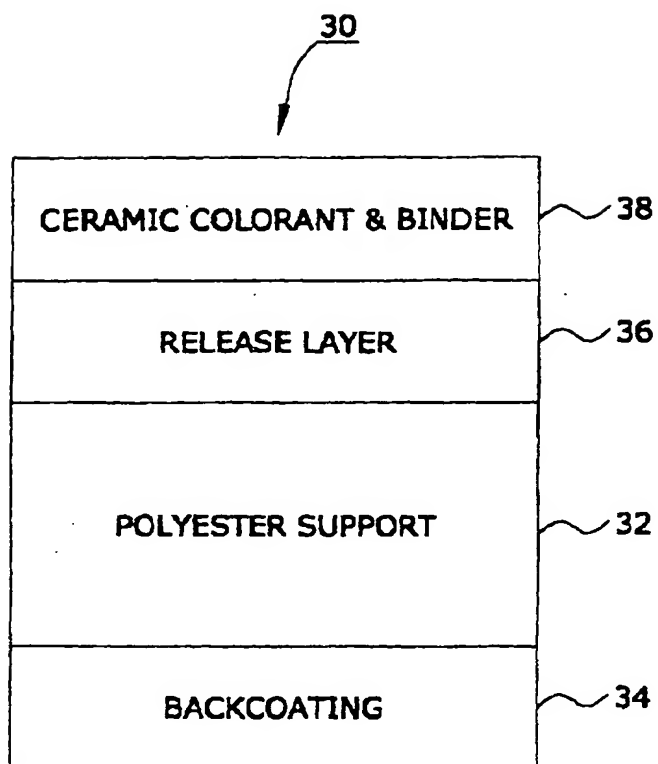


FIG. 2

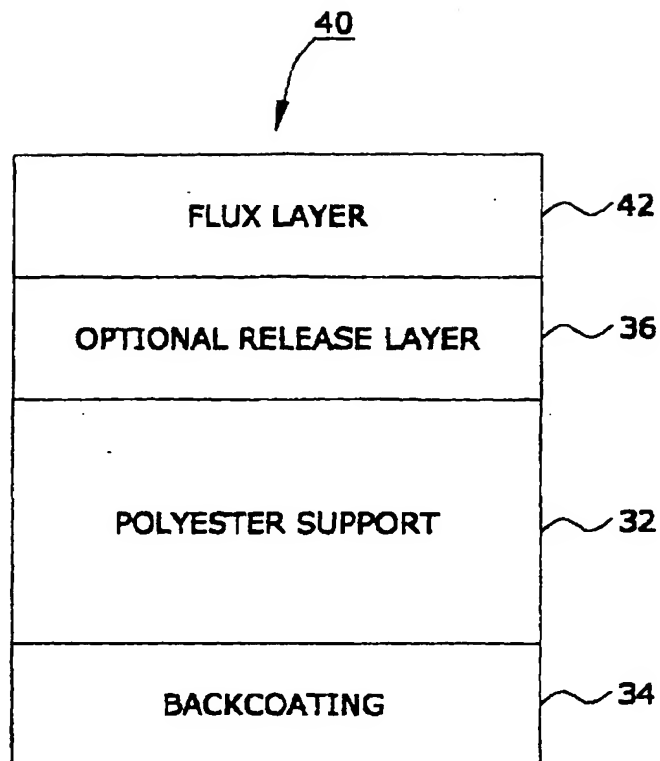
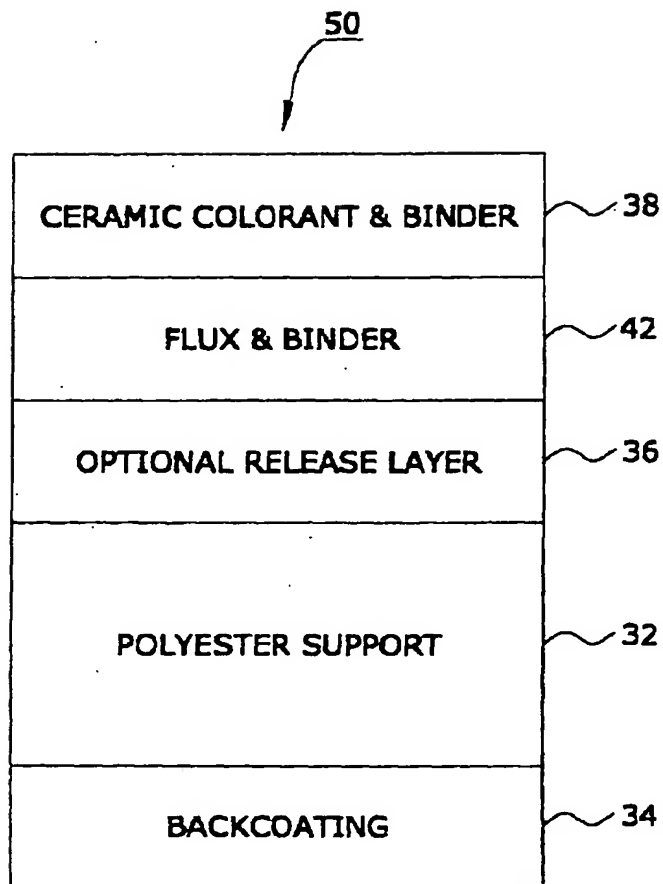


FIG. 3



**FIG. 4**



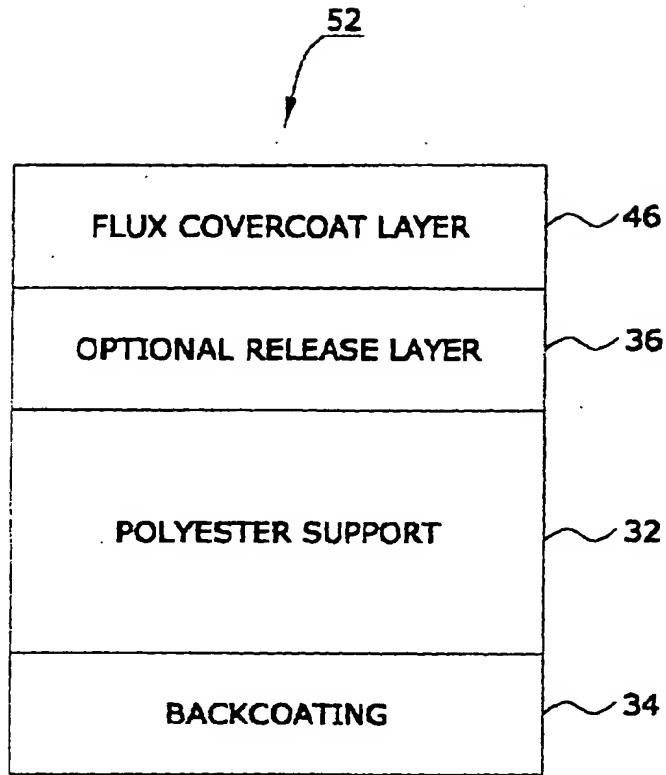


FIG. 5

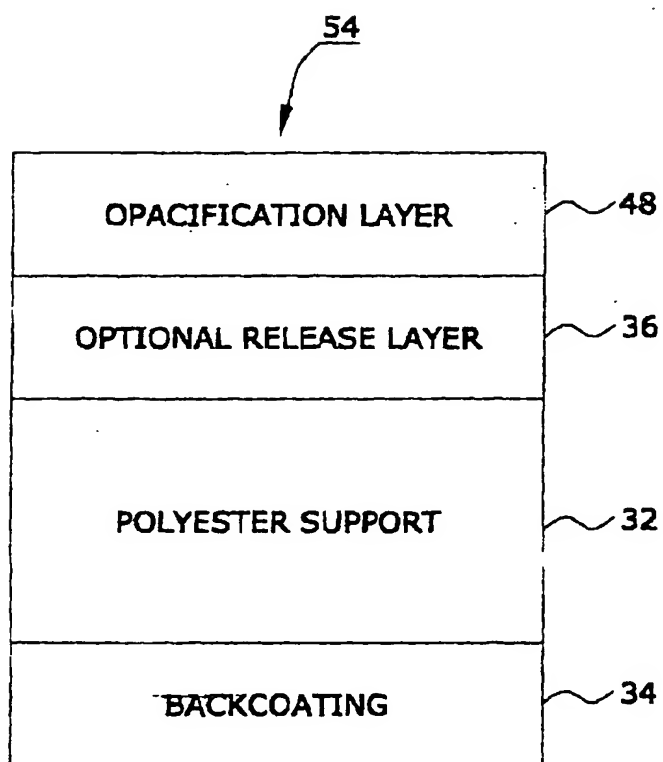


FIG. 6

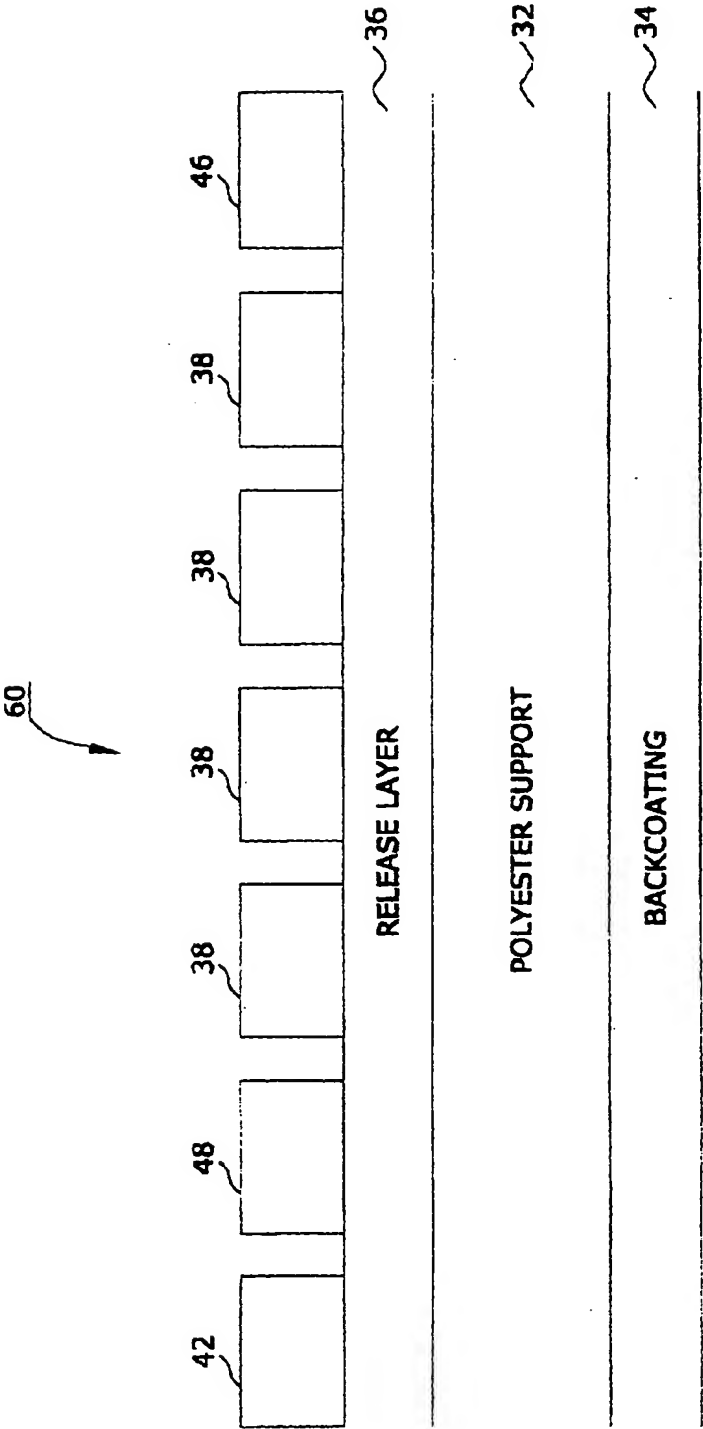
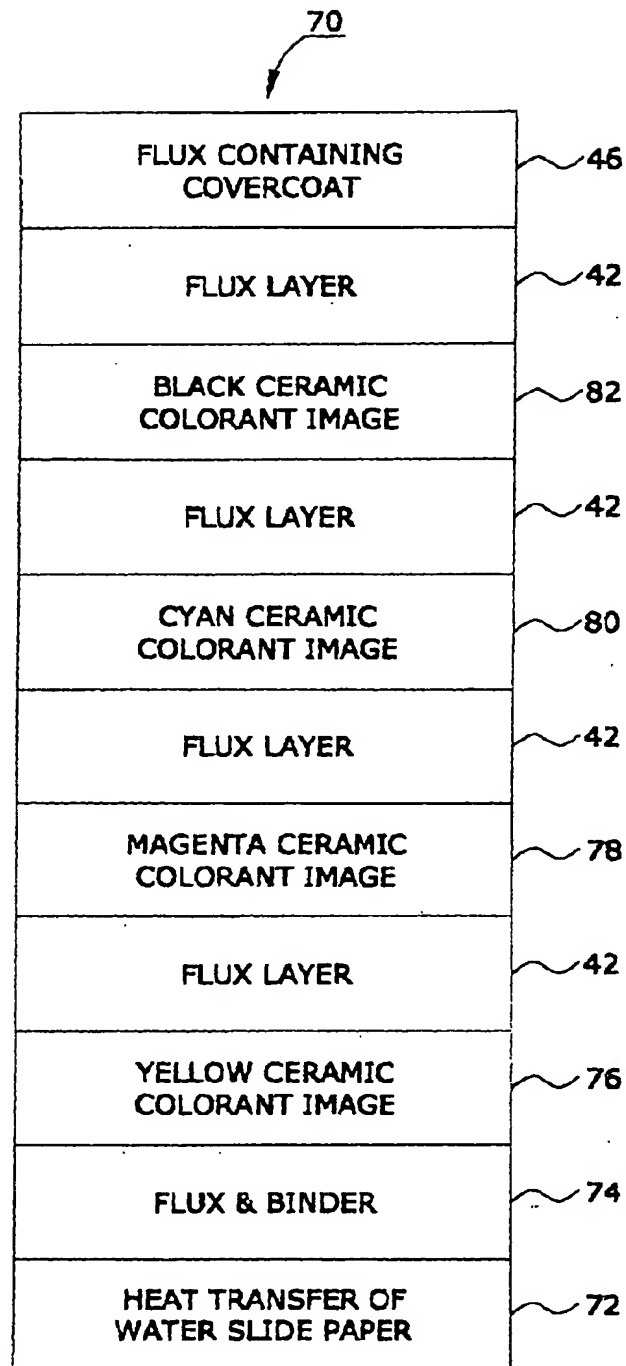


FIG.6A



**FIG. 7**

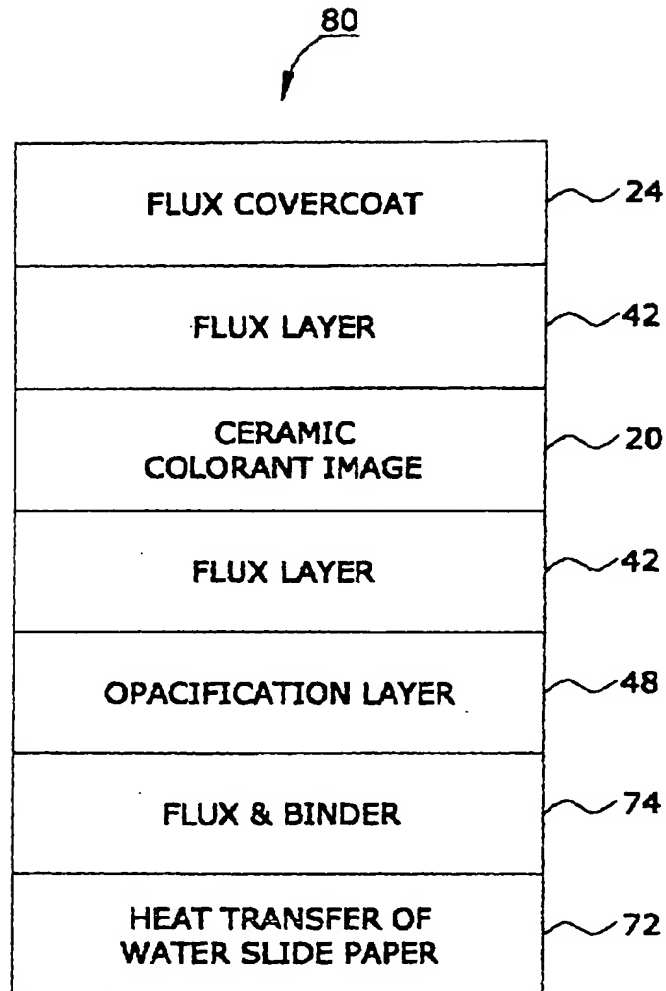
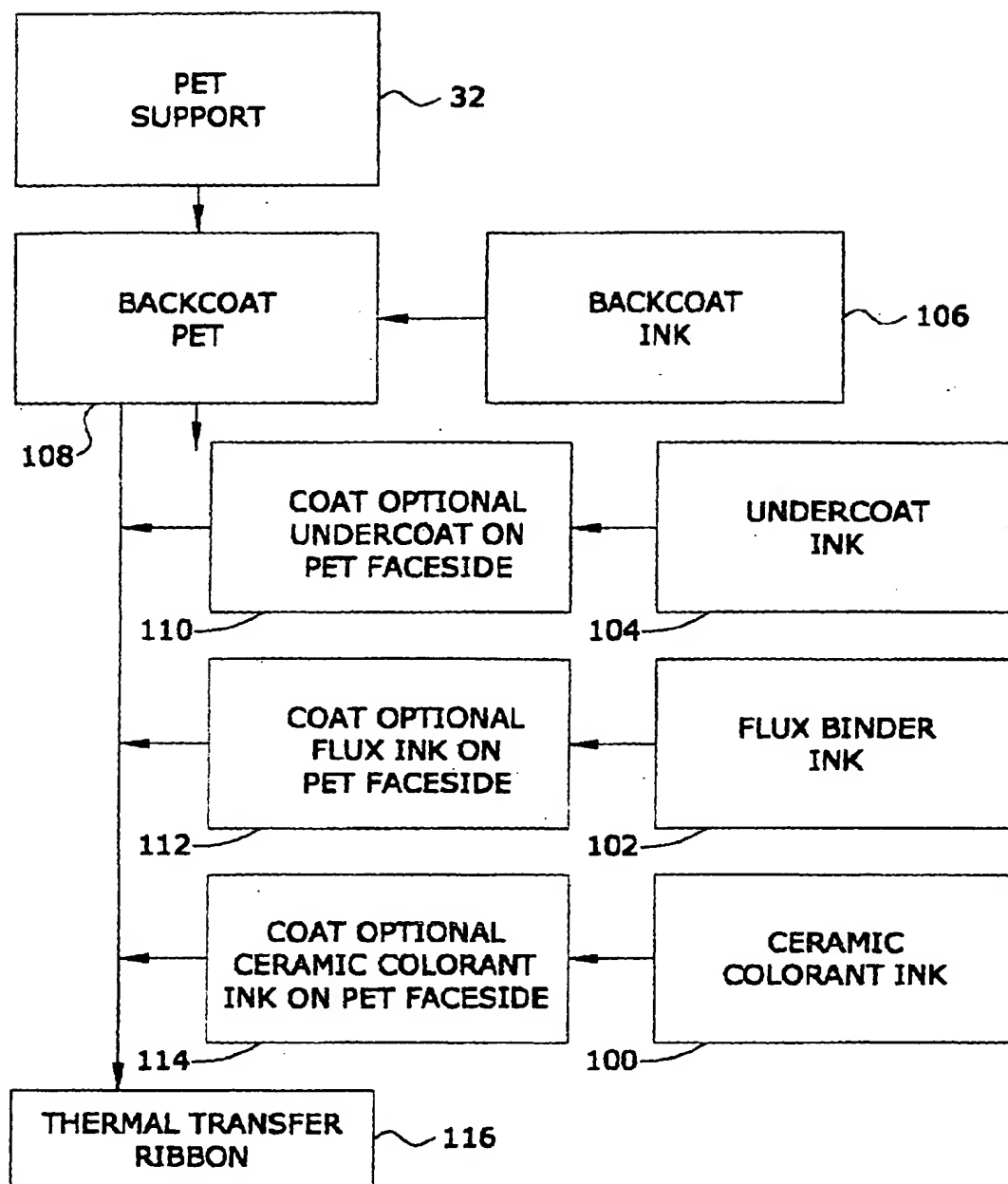
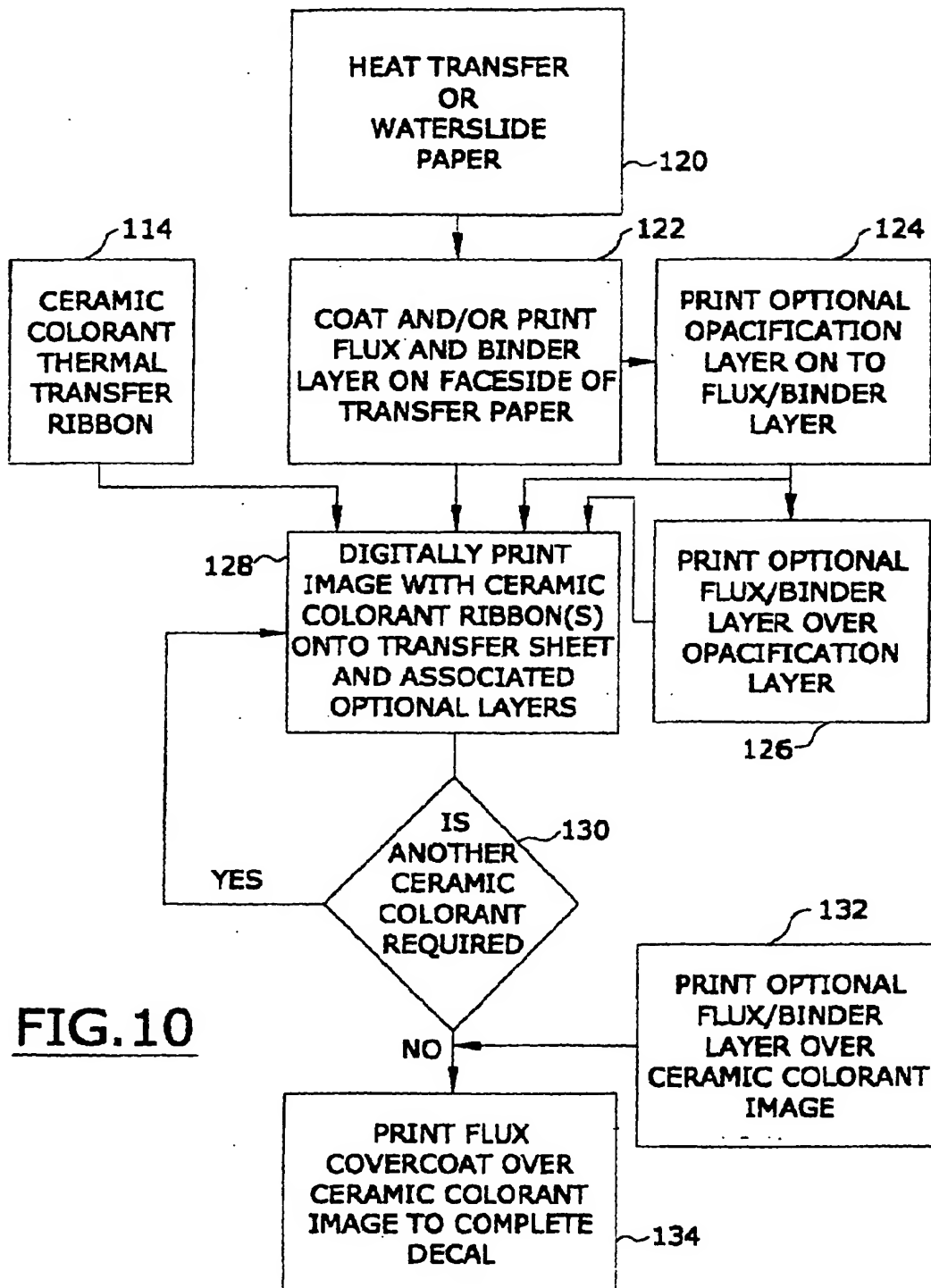
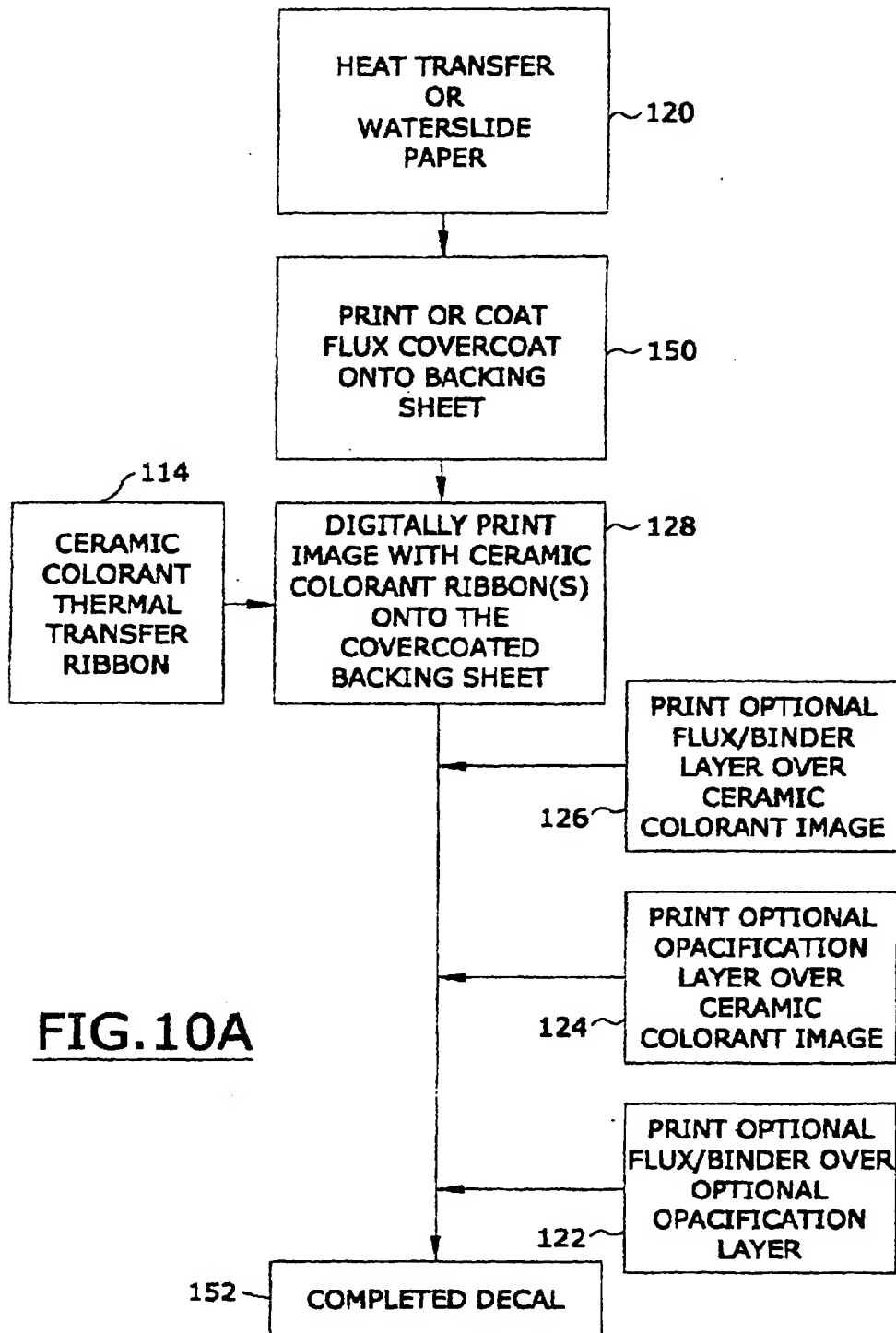


FIG. 8

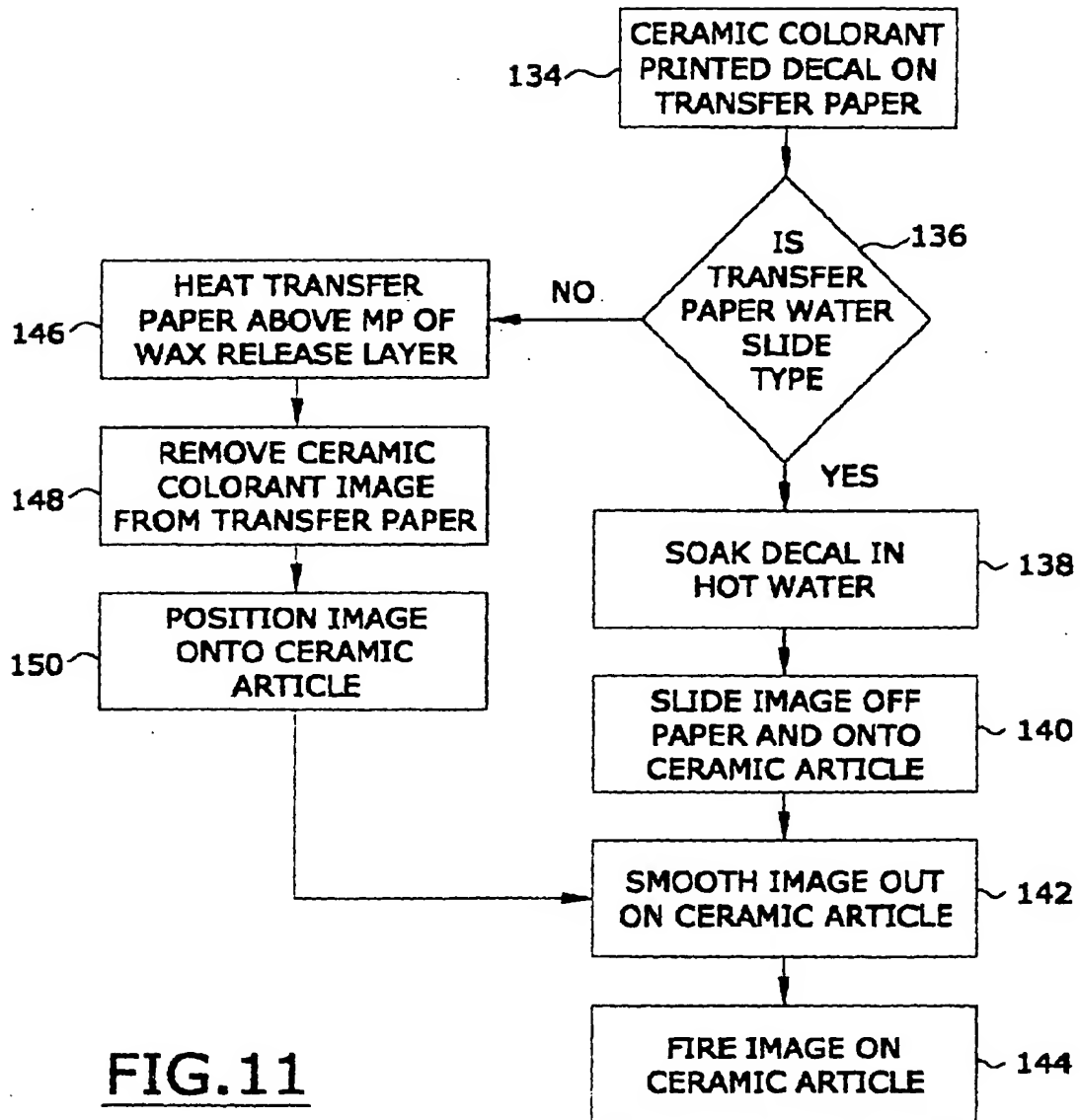


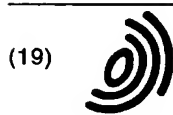
**FIG.9**







**FIG.11**



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 207 050 A3**

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:  
02.04.2003 Bulletin 2003/14

(51) Int Cl.7: **B44C 1/17**

(43) Date of publication A2:  
22.05.2002 Bulletin 2002/21

(21) Application number: **01309257.2**

(22) Date of filing: **31.10.2001**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR**  
Designated Extension States:  
**AL LT LV MK RO SI**

(30) Priority: **31.10.2000 US 702415**

(71) Applicant: **International Imaging Materials Inc.  
Amherst, NY 14228 (US)**

(72) Inventors:  
• **Geddes, Pamela A.**  
**Alden, New York 14004 (US)**  
• **Briggs, Barry J.**  
**Kelowna, British Columbia V1Z 3R3 (CA)**  
• **Harrison, Daniel J.**  
**Pittsford, New York 14534 (US)**

(74) Representative: **Powell, Stephen David et al  
WILLIAMS POWELL  
4 St Paul's Churchyard  
London EC4M 8AY (GB)**

(54) **Thermal transfer system for fired ceramic decals**

(57) A process for preparing a ceramic decal in which a printed image is applied to a backing sheet, and a covercoating is then applied to the printed substrate. A digitally printed ceramic colorant image is applied to the backing sheet; metal oxide colorant with a refractive index of greater than about 1.6 is used as the colorant.

Thereafter, the printed image is covercoated with an overcoat containing frit and binder. The total amount of frit applied in the process divided by the total amount of colorant used is at least 2, and the frit used has a melting temperature of at least 550 degrees Centigrade.

**EP 1 207 050 A3**



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 01 30 9257

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	WO 97 00781 A (ASHLEY MICHAEL DAVID ; RAWLINGSON ROBERT JOHN (GB)) 9 January 1997 (1997-01-09) * page 3, line 8 - page 5, line 1 * * claims 1-22 * ---	1-10	B44C1/17
A,D	US 5 132 165 A (BLANCO LOUIS A) 21 July 1992 (1992-07-21) * column 2, line 31 - line 39 * * column 3, line 5 - line 14 * * column 7, line 25 - line 49 * ---	1-10	
A	US 4 126 728 A (HOLLERAN LOUIS M ET AL) 21 November 1978 (1978-11-21) * column 2, line 64 - column 3, line 13 * ---	1-10	
A	US 5 989 636 A (WINE MICHAEL M) 23 November 1999 (1999-11-23) * column 5, line 15 - column 6, line 22 * ---	1-10	
A	WO 00 46043 A (CLARE ANDREW WALTER N ; CONTRA VISION LTD (GB); HILL ROLAND G (GB)) 10 August 2000 (2000-08-10) * page 28, line 29 - page 29, line 28 * ---	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.7) B44C B41M
A	EP 0 987 126 A (POLYCARTA LIMITED) 22 March 2000 (2000-03-22) * the whole document * -----	1-10	
The present search report has been drawn up for all claims			
Place of search: MUNICH		Date of completion of the search: 6 February 2003	Examiner: Mörsky, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 (03.02.2004)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 30 9257

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

06-02-2003

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 9700781	A	09-01-1997	AU	6133296 A	22-01-1997
			WO	9700781 A1	09-01-1997
			GB	2318090 A ,B	15-04-1998
US 5132165	A	21-07-1992	GB	2245221 A ,B	02-01-1992
US 4126728	A	21-11-1978	NONE		
US 5989636	A	23-11-1999	US	5693395 A	02-12-1997
WO 0046043	A	10-08-2000	AU	2822300 A	25-08-2000
			CA	2361546 A1	10-08-2000
			GB	2362607 A ,B	28-11-2001
			WO	0046043 A1	10-08-2000
EP 0987126	A	22-03-2000	EP	0987126 A2	22-03-2000

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82